Uranium Clusters

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Base-Driven Assembly of Large Uranium Oxo/Hydroxo Clusters**

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Control of actinide chemistry at the nanoscale is still at an early stage, despite the potential importance of nanostructured actinide materials as shown by some recent breakthroughs in the field.[1–3] Nanosized oxide and hydroxide clusters of actinides play an important role in technology for the nuclear industry, in the migration of the actinides released in the environment by mining, energy production or weapons, and into related remediation strategies.[4–7] Notably, although U^{VI} complexes are the major species involved in migration processes, the bacterial bioreduction of hexavalent uranium was shown to produce soluble molecular U^{IV} oxide clusters rather than insoluble UO_2. Nanoparticle formation is likely to impact uranium mobility and limit the efficiency of microbial reduction in actinide immobilization.[6,8] Soluble oligomeric hydroxide and hydrous oxides resulting from Pu(IV) hydrolysis are also responsible for the transport of plutonium in the environment.[4,9–12]

The chemistry of hydroxide and oxide clusters containing actinides in a reduced oxidation state (IV and V) can provide important information for understanding geochemical reactions and should lead to the isolation of actinide compounds with new topologies.[13] Furthermore, such clusters are currently of great interest as potential candidates in the design of catalysts or molecular magnets.[14,15]

However, in contrast with the wide variety of polyoxometalates reported for transition metals,[16] actinide cluster chemistry is in its infancy and the parameters controlling the assembly of large actinide clusters remain elusive. Recently the use of peroxide ligands has enabled the isolation from alkaline solutions of a fascinating series of large hexavalent uranyl clusters containing up to 60 uranium atoms.[2,17,18] A few oxide/hydroxide clusters containing uranium in the oxidation states IV and V have also been isolated over the years in aqueous or anhydrous conditions.[19–27] However, in contrast with the structural diversity of U^{VI} peroxide clusters, all these U clusters have a hexanuclear structure,[19–27] with the only exception being a dodecanuclear cluster reported by our group.[23] Although oxo/hydroxo clusters provide reasonable models for the actinide nanoparticles implicated in actinide migration, their reactivity remains unexplored. In particular, the intriguing possibility of using these small clusters as building blocks for the isolation of new cluster topologies has never been investigated. We have recently reported the stable $\{U_6O_8\}$ U^{IV} benzoate cluster $[U_6O_4(OH)_4(C_6H_5COO)_{12}(Py)_3]$.[26] Benzoate was used as a model for humic acids, which are known to enhance bioreduction of U^{VI} through the formation of soluble colloidal nanoparticles.[28]

Herein we show how organic bases can be used to control the size of the cluster assembly and we present the crystal structures of two new polyoxometalate clusters $[U_{10}O_8(OH)_6(PhCO_2)_{14}I_4(H_2O)_2(MeCN)_2]$ (**1**) and $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(C_6H_5COO)_{24}]\}\cdot 4\,MeCN$, (**3**) with unprecedented $\{U_{10}O_{14}\}$ and $\{U_{16}O_{24}\}$ topologies.

We have previously reported that the $[U_6O_4(OH)_4(C_6H_5COO)_{12}(Py)_3]$ cluster (Figure 1) is obtained in good yield from the stoichiometric reaction of uranium triiodide with water in acetonitrile in the presence of potassium benzoate (with a benzoate/uranium ratio of 2:1) after addition of pyridine.[26] ^1H NMR studies show that the addition of pyridine to the acetonitrile reaction mixture leads to large changes in the NMR spectrum (changing from broad to well-defined signals assigned to the $\{U_6O_8\}$ cluster), suggesting that pyridine has an important role in the formation/isolation of the $\{U_6O_8\}$ benzoate cluster.

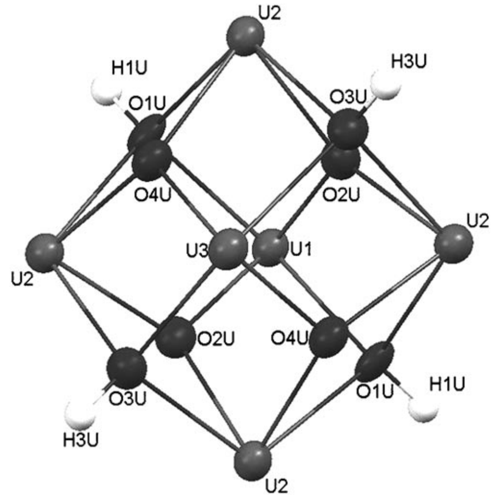

Figure 1. The $\{U_6O_4(OH)_4\}$ core in the $[U_6O_4(OH)_4(C_6H_5COO)_{12}(Py)_3]$ benzoate cluster from Ref. [26].

We have now isolated green X-ray quality crystals of $[U_{10}O_8(OH)_6(PhCO_2)_{14}I_4(H_2O)_2(MeCN)_2]$ (**1**) and $[U_{10}O_8(OH)_6(PhCO_2)_{12.79}I_{3.2}(H_2O)_4(MeCN)_4]_2I\cdot 4\,MeCN$ (**2**) from the acetonitrile reaction mixture resulting from the

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stoichiometric hydrolysis of $[UI_3(thf)_4]$ in the presence of benzoate. The structure of the neutral cluster $[U_{10}O_8(OH)_6(PhCO_2)_{14}I_4(H_2O)_2(MeCN)_2]$ **1** is shown in Figure 2 (the structure of **2** is shown in the Supporting Information, Figure S7).

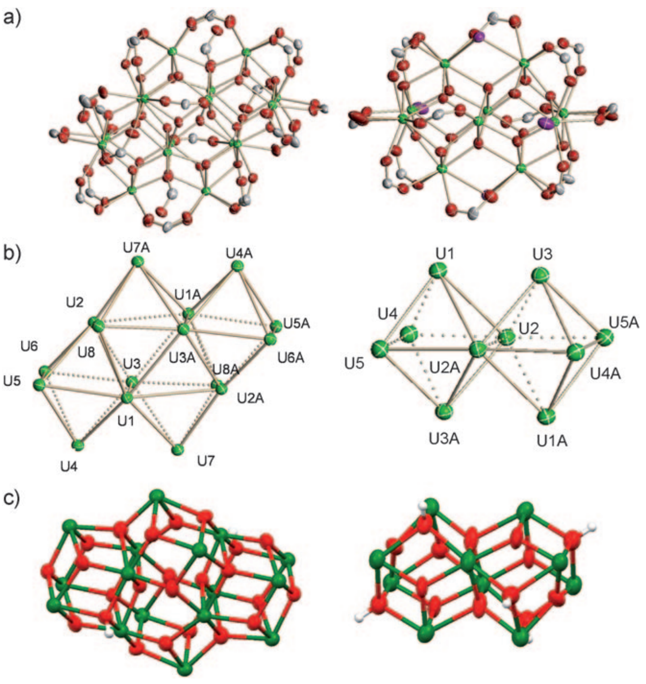


Figure 2. a) The structure of **1** (right) and **3** (left). Ellipsoids are set at 30% probability; H atoms, acetonitrile molecules, and the benzoate phenyl groups are removed for clarity. b) The uranium arrangement in **1** (right) and **3** (left). Ellipsoids are set at 30% probability. c) Detail of the $\{U_{10}O_8(OH)_6\}$ core in **1** (right) and of the $\{U_{16}O_{22}(OH)_2\}$ core in **3** (left). Ellipsoids are set at 50% probability. Average bonds lengths [Å] for **1**: U–O 2.20(10), U–OH 2.43(6), U–OH_2 2.90(4), U–O(benzoate) 2.37(3), U–U 3.83(6). **3**: U–O 2.30(10), U–O(benzoate) 2.42(6), U–U 3.71(7). U green, O red, C gray, I purple, H white.

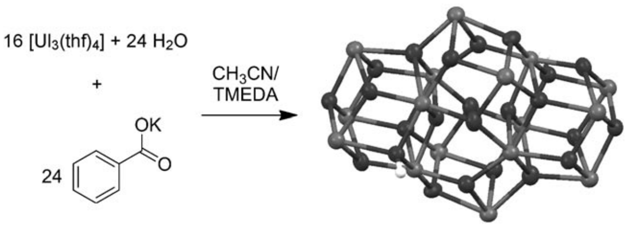
The X-ray crystal structures of **1** and **2** reveal the presence of discrete decanuclear oxo/hydroxo clusters with $\{U_{10}O_{14}\}$ cores. The two structures differ in the number of benzoate ligands decorating the $\{U_{10}O_{14}\}$ core with a ratio of benzoate ligand to uranium of 1.4:1 in **1** and 1.3:1 in **2**. Moreover, the structure of **2** (see the discussion in the Supporting Information) is disordered, with partial occupation of iodide and benzoate ligands suggesting the presence of a mixture of clusters in the solid state with a $\{U_{10}O_{14}\}$ core having a variable ratio of benzoate/iodide ligands.

The structure of **1** consists of 10 uranium atoms connected together by bridging oxides (8), hydroxides (6), and benzoate ligands (14) with five crystallographically different uranium ions. The cluster size is about $20\times20\times23$ Å^3, with the largest U−U distance being 8.6 Å. The geometrical arrangement of the 10 uranium atoms can be described as two octahedrons sharing the edge formed by the two symmetry-related U2 ions (inversion center located in the middle of the common edge). Three triply bridging oxides and three triply bridging hydroxides alternatively cap six faces of each octahedron. The four remaining faces share two μ_4 oxides bridging the two adjacent octahedrons. The calculated bond valence sum (BVS) is in agreement with the presence of 6 hydroxide and 8 oxide oxygen atoms. The value of the mean U−O distances are 2.23(5) Å for the μ_3-O, 2.43(6) Å for the μ_3-OH, and 2.40(1) Å for the two μ_4-O atoms. Six benzoate ligands bridge six external edges of each octahedron while two additional benzoates bridge the U1 and U3 atoms connecting the two octahedrons. A bridging iodide connects U1 and U3 at the vertex of each octahedron (a second iodide bridges the symmetry-related U1 A and U3 A atoms). The presence of 8 oxo ligands, 6 hydroxo ligands, 14 benzoates, and 4 iodides adds up to an overall charge of +40 for complex **1**, which, distributed over 10 uranium centers, gives an average positive charge of +4. The calculated BVS is in agreement with the presence of 10 U^{IV} ions. One acetonitrile molecule is also found in the coordination sphere of U2 and U2 A, and a water molecule in that of U5 and U5A(2).

Crystals of **1** and **2** were both obtained reproducibly from the hydrolysis reaction of $[UI_3(thf)_4]$ with stoichiometric amounts of water, even in the presence of different benzoate/uranium ratios, suggesting that only clusters with $\{U_{10}O_8(OH)_6\}$ core are present in acetonitrile solution. Pyridine probably plays two different roles in the formation of the $[U_6O_4(OH)_4(C_6H_5COO)_{12}(Py)_3]$ cluster from the $\{U_{10}O_8(OH)_6\}$ clusters. The higher coordinating ability of pyridine with respect to acetonitrile is likely to favor smaller size clusters. Moreover, the basicity of pyridine could play an important role in favoring the deprotonation of coordinated water molecules to yield hydroxo and oxo groups. Notably in cluster **1** two water molecules remain coordinated to the uranium atoms while in the U_6O_8 cluster only oxo and hydroxo groups are found.

To confirm that organic bases can be used to tune the final cluster topology in the hydrolysis reaction and to further elucidate the influence of the nature of the base, we performed the hydrolysis reaction in the presence of the stronger organic base TMEDA (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine; Scheme 1). Green crystals of $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(C_6H_5COO)_{24}]\}\cdot4\,MeCN$ (**3**) were isolated after addition of TMEDA to an acetonitrile solution of $[UI_3(thf)_4]$ reacted with 1.5–2 equivalents of water and 2 equivalents of potassium benzoate. Compound **3** is the largest oxo/hydroxo cluster of uranium reported to date.

The X-ray crystal structure of **3** shows the presence of a discrete oxo/hydroxo cluster with a $\{U_{16}O_{24}\}$ core and with a 1.5:1 benzoate/uranium ratio (Figure 1). Thus the reaction of



Scheme 1. Synthesis of cluster **3**. The $\{U_{16}O_{22}(OH)_2\}$ core is shown; U gray, O black, H white.

stoichiometric amounts of water (1.5–2 equiv) with [UI_3(thf)$_4$] followed by addition of 1.5 equivalents of potassium benzoate and TMDEA allows the reproducible synthesis of **3** in 80 % yield.

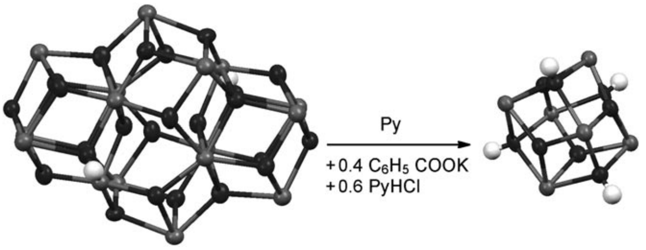
The geometrical arrangement of the 16 uranium atoms in the structure of **3** can be described as consisting of four fused octahedrons with eight crystallographically inequivalent uranium atoms related to their symmetry equivalents by an inversion centre (located in the middle of the U1–U1 A edge). The overall cluster size is approximately 24 × 24 × 26 Å^3 while the core structure is 11.13 Å wide (U6–U6 distance) and 8.38 Å high (U8–U8 distance). The two external octahedrons share one edge with each one of the two adjacent octahedrons. Each octahedron shares one edge with all neighboring octahedrons (for the idealized structure, see the Supporting Information, Figure S8). The U1, U2, and U3 atoms are seven-coordinate with a distorted monocapped trigonal prism geometry while the remaining uranium atoms are eight-coordinate with a distorted square antiprism geometry. The uranium atoms are connected by 22 oxo, 2 hydroxo, and 24 benzoate ligands. 16 μ_3-O ligands, 2 μ_3-OH ligands, and 6 μ_4-O ligands cap 28 triangular faces of the octahedrons; four μ_4-O (Supporting Information, Figure S9) are located in the tetrahedral cavity formed by two or three adjacent octahedrons. Only the four triangular faces in the core of the structure are not capped by oxo groups, which is probably due to steric constraints. As a result, the geometry of two core octahedrons is highly distorted, with the U1–U1 A edge being much longer (4.89 Å) than the other edges (mean value of 3.72(7) Å). Finally, two μ_4-O groups each bridge three uranium atoms (U1, U4, U5) and a potassium cation. The calculated BVS for the uranium atoms is in agreement with the presence of 12 U ions in the +IV oxidation state and 4 U ions in the +V oxidation state (localized on U2 and U3). U^{IV}/U^{V} mixed-valent clusters with a $U_{12}O_{20}$ and U_6O_8 core have been previously isolated using triflate ligands,[23] but the calculated BVS suggested the presence of delocalized valence clusters. Mixed-valent polyoxometalates with localized or delocalized valence are well known for d-block metals and can lead to interesting magnetic properties arising from the interplay of exchange and delocalization effects.[16]

As two potassium cations are also present in the structure, an overall positive charge of 70 results for cluster **3**, which is consistent with the presence of 2 hydroxo and 22 oxo groups in the neutral complex. The mean U–O distances is 2.3(1) Å for the μ_3-O groups, 2.4(1) Å for the μ_4-O groups, and 2.29(9) Å for the μ_3-OH groups. The position of the two hydroxo groups in the crystal structure has been assigned on the basis of the geometric parameters. The calculated BVS value for the oxygen atoms is rather high (1.7), but is lower than the BVS for the other oxygen atoms. There are no interactions in the lattice, which could justify the presence of a oxo group with a low BVS value. The 1.7 value could be ascribed to a delocalization of the position of the hydroxo hydrogen atoms. The presence of hydroxo groups was confirmed by the IR spectrum, which has a low-intensity band centered at 3599 cm^{-1} that is assigned to the O–H stretching mode. The presence of U^{IV} was confirmed by the presence of the typical band[29] at about 690 nm in the UV/Vis spectrum.

The solid-state magnetic susceptibility χ_M of the U_{16} cluster **3** was measured in the temperature range 2–300 K in a 2 T field, and the resulting effective magnetic moment (μ_{eff}) is plotted versus T (Supporting Information, Figure S13). The μ_{eff} value at 300 K (2.89 μ_B) is slightly lower than the value calculated for 12 U^{IV} and 4 U^{V} behaving as independent paramagnets ($\mu_{eff} = 3.32\ \mu_B$), but is similar to the magnetic moment (2.79 μ_B) reported for the mixed valence cluster [$U_{12}(\mu_3\text{-OH})_8(\mu_3\text{-O})_{12}I_2(\mu_2\text{-OTf})_{16}(CH_3CN)_8$] containing ten U^{IV} and two U^{V}.[23] Such clusters may present magnetic exchange coupling but a more accurate analysis of the magnetic properties is beyond the current understanding of the interplaying effects of temperature independent paramagnetism, crystal-field splitting, spin–orbit coupling, and orbital angular momentum quenching in such complex uranium systems.[30]

The formation of the {$U_{16}O_{22}(OH)_2$} cluster **3** from [UI_3(thf)$_4$] hydrolysis in the presence of TMDEA compared to the formation of the cluster [$U_6O_4(OH)_4(C_6H_5COO)_{12}(Py)_3$] in pyridine or to the mixture of {$U_{10}O_8(OH)_6$} species in the absence of bases, demonstrates the important role of the base and of its nature in the outcome of the hydrolysis reaction.

Moreover, proton NMR and UV spectroscopic studies show that the {$U_{16}O_{22}(OH)_2$} cluster **3** is converted into the {$U_6O_4(OH)_4$} cluster after addition of PyHCl (0.6 equiv) to a pyridine solution of **3** in the presence of potassium benzoate (Scheme 2). Thus acidic conditions and coordinating solvents favor the formation of smaller clusters, while the formation of larger clusters is favored by strong bases promoting the deprotonation of hydroxo groups to afford oxo ligands.



Scheme 2. Reaction of the {$U_{16}O_{22}(OH)_2$} core of **3** with PyHCl in pyridine. U gray, O black, H white.

In conclusion, we have isolated two new large uranium oxo/hydroxo clusters with original topologies from the stoichiometric hydrolysis of trivalent uranium in the presence of the benzoate and iodide ligands. These nanosized oxides provide useful models for understanding the chemistry of bulk oxides or colloids.[13] These results also show that the topology of the final cluster assembly can be tuned by a careful choice of solvent and base conditions, thus providing a tool for the nanoscale control of uranium materials. Finally the isolation of aggregates with $U_{10}O_{14}$ and $U_{16}O_{24}$ cores clearly demonstrates that polyoxometalates containing U^{IV} and/or U^{V} are not limited to the U_6O_8 topology and that a wide variety of different new topologies are yet to be discovered.

Experimental Section

3: A 0.5 M solution of water in acetonitrile (660 μL, 0.33 mmol) was added dropwise under vigorous stirring to a dark-green solution of $[UI_3(thf)_4]$ (200 mg, 0.22 mmol) in MeCN (4 mL), resulting in a color change to light green after 5 min of stirring. A suspension of potassium benzoate (53.0 mg, 0.33 mmol) in acetonitrile (2 mL) was added to the solution. The light-green reaction mixture was stirred over 16 h and then filtered to remove KI. *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA; 100 μL) was added to the resulting solution, leading to the rapid precipitation of a light-green microcrystalline powder. The microcrystalline powder was isolated by centrifugation, washed with acetonitrile (2 × 1.5 mL), and dried to yield complex **3** (82 mg, 0.011 mmol, 80 %). X-ray-quality crystals were obtained either by letting a dilute acetonitrile solution of **3** (0.3 mmol) stand or by slow diffusion of an acetonitrile solution of TMEDA into a solution of $[UI_3(thf)_4]$ that had already reacted with H_2O (1.5 equiv) and potassium benzoate (1.5 equiv).

The measured IR spectra of the microcrystalline and single crystals are identical. Elemental analysis calcd (%) for **3** ($C_{180}H_{140}N_6O_{72}K_2U_{16}$, $M_r = 7425.66$): C 29.12, H 1.90, N 1.13; found C 28.99, H 2.00, N 1.16.

CCDC 813202 (**1**), CCDC 813203 (**2**), and CCDC 813204 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. Figure Graphics are generated using MERCURY 2.3 Supplied with Cambridge Structural Database; CCDC: Cambridge, U.K., 2004–2009.

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